

AD-A163 448 INNOVATIVE SOLIDIFICATION TECHNIQUES FOR HAZARDOUS
WASTES AT ARMY INSTALLATIONS(U) ARMY ENGINEER WATERWAYS
EXPERIMENT STATION VICKSBURG MS ENVIR. T E MYERS
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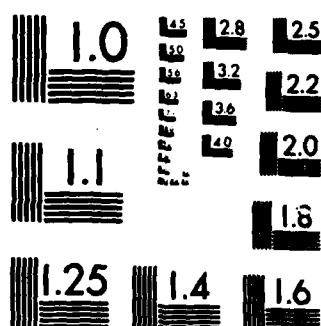
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INNOVATIVE SOLIDIFICATION TECHNIQUES FOR HAZARDOUS WASTES AT ARMY INSTALLATIONS

by

Tommy E. Myers

Environmental Laboratory

DEPARTMENT OF THE ARMY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report presents the results of a laboratory investigation of solidi- fication processing of Basin F liquid from the Rocky Mountain Arsenal (RMA), Denver, Colo. The residuals in Basin F contain toxic metals that require treat- ment and disposal. Innovative techniques for immobilization of contaminants in hazardous wastes such as Basin F liquid are needed. The contaminant immobili- zation technique described herein could provide the disposal technology needed to (Continued)		

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20. ABSTRACT (Continued).

immobilize toxic metals. Due to the developmental nature of the technology described, additional testing will be required before the technique is adopted.

The basis of the technique is adsorption of toxic metals to soil that has been conditioned with N-(~~B~~-aminoethyl)-~~gamma~~-aminopropyl-trimethoxysilane (organosilane). Conditioning with this organosilane improved the metal sorption characteristics of the soil used as a solidification additive. The ultimate adsorption capacity was improved from 6.6 to 15.2 mg copper per gram or sorbent, and the Langmuir distribution coefficient was increased from 0.0229 to 0.0265 l/mg.

Basin F liquid was treated by first mixing the liquid with soil in order to adsorb copper. The resulting slurry was solidified using flyash and lime as setting agents. In order to investigate chemical leaching characteristics, leaching tests were run on two types of solidification products. One product was prepared using soil to adsorb copper, and the other was prepared using organosilane-conditioned soil as the sorbent. The leaching tests showed that organosilane conditioning of the soil additive lowered the leachability of copper from solidified Basin F liquid.



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PREFACE

This report presents the results of a laboratory investigation of solidification of Basin F liquid from the Rocky Mountain Arsenal (RMA), Denver, Colo. The residuals in Basin F are hazardous wastes that require treatment and disposal. Innovative techniques for immobilization of contaminants in hazardous wastes such as Basin F liquid at Army installations are needed. With the proper development, the contaminant immobilization systems described herein could provide the disposal technology needed to immobilize one class of contaminants, toxic metals. Due to the developmental nature of the technology described, additional testing and evaluation are recommended before the technology is adopted for field-scale application.

This report was written by Mr. Tommy E. Myers, Water Supply and Waste Treatment Group, Environmental Laboratory (EL), US Army Engineer Waterways Experiment Station (WES), as his masters thesis at Mississippi State University, Starkville, Miss. The thesis research was sponsored by the Department of Army In-House Laboratory Independent Research (ILIR) program, ILIR Project No. 4A161101A91D. Analyses were performed by the Analytical Laboratory Group, EL. Mr. Norman R. Francingues, Jr., was the immediate supervisor on the project. Overall direction came from Mr. Andrew J. Green, Chief, Environmental Engineering Division, EL, and Dr. John Harrison, Chief, EL. Ms. Jamie W. Leach of the WES Publications and Graphic Arts Division edited the report.

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INNOVATIVE SOLIDIFICATION TECHNIQUES
FOR HAZARDOUS WASTES AT ARMY INSTALLATIONS

PART I: INTRODUCTION

Research Need

1. Protection of the environment through regulation of waste disposal is authorized in various laws of the United States. The Resource Conservation and Recovery Act of 1976 (RCRA) was the first comprehensive act to regulate hazardous wastes. It specifically requires compliance by all Federal agencies and does not exempt military activities. Under RCRA, contract disposal does not absolve the hazardous waste generator of the legal liabilities associated with improper disposal. Even though one party may contract with a second party to dispose of a hazardous waste, liability is not transferable under RCRA, and the first party, as waste generator, is still liable for damages resulting from improper disposal. Hence, the Department of Army (DA) is responsible for the safe and proper disposal of hazardous wastes generated at DA facilities.

2. Hazardous wastes containing toxic metals are generated at Army facilities as by-products of manufacturing operations, as sludges from waste treatment processes, by accidental spills, by equipment rehabilitation processes, and from past improper disposal practices. Innovative technologies developed for treatment of metal contaminants have Army mission relevancy as follows: (a) prevention of further degradation of the environment, (b) compliance with present and future environmental regulations, (c) reduction of waste disposal costs, and (d) avoidance of disruption to readiness operations.

3. Some DA installations have serious disposal problems (Chesler 1982). Metal sludges produced in the treatment of wastewater from metal cleaning, metal finishing, and metal plating operations, for example, are specifically listed in Title 40 Code of Federal Regulations 261 (40 CFR 261) as hazardous wastes. RCRA requires that these wastes either be detoxified, landfilled in a RCRA-permitted facility, or delisted (determination of nonapplicability of RCRA regulations). Short of nuclear fusion, there are no known techniques for detoxification of most metals. Offsite disposal in an RCRA landfill is

expensive and can be prohibitive unless the volume of waste is small and the haul distance is short. Due to the time and expense involved in obtaining permits and in constructing and operating an RCRA landfill, onsite RCRA landfilling is not cost-effective in many situations. Delisting involves petitioning the Administrator of the Environmental Protection Agency (EPA) for a determination of nonapplicability. The petitioner must show that the waste can be disposed of outside of an RCRA landfill without significant environmental impact. To date (1985) no metal wastes from DA facilities have been delisted.

4. The optimal solution for each hazardous waste disposal problem is highly dependent on site-specific factors. Waste generation rate, waste character and physical condition, and location of the generating facility are some of the parameters influencing the selection of an optimum disposal option. For small quantities, contracted offsite disposal will probably continue to be the best solution. For large waste quantities a more economical method of waste disposal involving delisting is needed. Higher contract disposal costs and less availability of hazardous waste landfills are anticipated. In order for delisting to be a practical alternative for toxic metal wastes generated at Army installations, innovative treatment techniques that immobilize metal contaminants are needed.

5. This report describes an innovative method for improving the metal immobilization efficiency of solidification processes used to treat hazardous wastes. The basis of the technique is adsorption and/or chemisorption of metals to a sorbent that is used in conjunction with solidification to immobilize toxic metals. The technique was applied to a DA hazardous waste, Basin F liquid at the Rocky Mountain Arsenal, Denver, Colo., using a sorbent prepared by conditioning soil with N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane.

Objectives and Approach

Objectives

6. The major objective of this study was to investigate the feasibility of reducing the metal leaching potential of solidified Basin F liquid by conditioning selected solidification additives with N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane. Specific objectives were as follows:

- a. Determine which additive (soil or flyash) in a soil/flyash/lime solidification process provides the organosilane-additive combination with the best sorption characteristics.
- b. Investigate the effect of selected organosilane-additive bonding procedures on metal sorption characteristics.
- c. Compare the leaching characteristics of solidified Basin F liquid processed using solidification additives with and without organosilane conditioning.

Approach

7. The research approach consisted of: (a) conducting a series of copper adsorption isotherm tests on various organosilane-additive preparations in order to determine which has the best sorption characteristics for copper, and (b) conducting a series of laboratory leaching tests on solidified waste prepared with and without silane conditioning of selected solidification additives.

PART II: BACKGROUND

Solidification

8. Solidification processing is a treatment technology that is sometimes applied to liquids and semisolids that are too toxic for biological treatment, too low in energy value and/or too corrosive for incineration, and too dilute for landfilling. Solidification typically involves mixing a setting agent(s) with a waste to form a hard, durable product that is substantially insoluble in water and in which the waste contaminants are entrapped in the solidified mass. There are several commercially available waste solidification systems in use in the United States (Malone, Jones, and Larson 1980). The most common setting agents are portland cement, flyash, kiln dust, lime, soluble silicates, gypsum, and combinations of these materials. Generic descriptions of the commercially available solidification processes have been published by Malone and Jones (1979).

9. Solidification typically provides three major advantages over raw waste management and disposal: (a) removal of free liquid, (b) development of structural integrity, and (c) improved contaminant isolation and containment (Mahloch, Averett, and Bartos 1976; Malone and Jones 1979; Malone, Jones, and Larson 1980). Isolation and containment of hazardous constituents are accomplished by waste entrapment in a cemented matrix and by conversion of waste constituents to less soluble compounds. Unfortunately, these mechanisms do not always prevent the leaching of hazardous constituents. The effectiveness of the entrapment mechanism depends on the permeability and durability of the solidified product. Because certain waste constituents can interfere with the setting reactions responsible for the development of a hardened mass, there may be problems with durability. Insoluble products from precipitation can be resolubilized if leaching conditions are different from the conditions in which precipitation took place. In particular, pH and oxidation-reduction potentials can be altered by percolating water to resolubilize toxic metals. In addition, not all materials are insoluble under the pH and redox conditions present in moist concrete or pozzolan. Hence, contaminants that have been simply entrapped or precipitated can be leached from solidified waste in varying degrees, depending on the type of waste, the kind of additives used for

solidification, and the environmental conditions of the disposal site (Malone and Larson 1983).

Sorbent-Assisted Solidification

10. Sorption of metals by soils and by organic chelating agents is one means by which toxic metals can be removed from contaminated water (Griffin et al. 1976; Korte et al. 1975, 1976; Fuller et al. 1980). Adsorption is thought to occur by two processes: physical attraction of substances to sorbent surfaces and chemical bonding of contaminants to sorbent surfaces (Metcalf and Eddy, Inc. 1979). If the bonds are weak as in physical attraction, then physical adsorption is said to have taken place. If the bonds that form are strong, then chemical absorption or chemisorption is said to have taken place. The terms "adsorption" and "physical adsorption" are used interchangeably. Adsorption is characterized as being reversible, and includes such mechanisms as attraction by van der Waals forces (physical attraction) and ion-exchange reactions (electrical attraction). Since adsorption is reversible, desorption will occur to some extent depending on the relative affinity of the contaminant for the aqueous phase versus the sorbed phase. The thermodynamics of the sorption system partition the contaminant mass between aqueous and adsorbed phases so that the contaminant is never all in one or the other phase, and thus cannot be released all at one time. Consequently, the amount released and especially the release rate are reduced if the contaminant is adsorbed to a solid phase, rather than simply entrapped in a lattice work as a soluble or sparingly soluble salt. Chemisorption is generally thought of as chemical bonding of a contaminant to the sorbent surface, as opposed to physical adsorption. It is characterized as being irreversible or only slightly reversible. Contaminants that have been attached by chemisorption show significant reduction in leaching potential.

11. Unfortunately, the solid matrix provided by cement- and pozzolan-based solidification processes has little or no sorption potential. However, if a sorbent incorporated into the crystalline matrix provided by solidification is included in the process formulation, then the potential for contaminant release from the solidified waste should be significantly reduced. With proper development, sorbent-assisted solidification could represent an improved treatment technology for toxic metal wastes.

12. One readily available and proven sorbent is soil, especially fine-grained soils that contain clay minerals. Most fine-grained soils adsorb both metal and organic pollutants (Jenne 1968; McCarty, Reinhard, and Rittmann 1981; Salim 1983; Schellenberg, Leuengerger, and Schwarzenbach 1984; Voice and Weber 1983). Most of the sorption capacity of soils is provided by the clay fraction. Moore, Godbee, and Kibbey (1976) used various clay minerals to improve the retention of radionuclides in cementitious grouts. Natural sorbents are particularly amenable to incorporation into solidification processing because the soil or clay particles provide filler that becomes part of the crystalline structure of the solidified product. As a filler, natural sorbents, such as soil, reduce the amount of primary setting agent(s) required to solidify waste. The use of soil in a solidification process does add bulk that occupies space in a landfill. In practice the reduction in cost of primary setting agent(s) usually does not offset the cost of landfilling the added bulk. However, consideration of the soil additive as only a filler does not take into account the value of the soil as a sorbent that assists in the immobilization of contaminants.

13. The sorption properties of soils and other materials can be improved by bonding to them certain organosilanes that have the ability to chelate metals. Silanes are a special family of silicon compounds derived from silane, SiH_4 . Organosilanes are xenobiotic (do not occur naturally) silane derivatives that possess important properties used by the chemical industry to improve the wetting or adhesion characteristics of materials (Arkles 1977). As chelating agents, some organosilanes have the ability to seize metal ions and sequester them from further reaction. A chelating molecule forms coordinate bonds between the metal ion and usually either a nitrogen, oxygen, or sulfur atom on the chelate molecule (Sawyer and McCarty 1978). Leyden and Luttrell (1975) used the metal-chelating properties of organosilanes to preconcentrate dissolved metals prior to chemical analysis by X-ray fluorescence. Malone and Karn (1982) reported the usefulness of an organosilane-silica gel sorbent in removing cadmium, chromium, copper, and zinc from metal-contaminated wastewater. Organosilanes can be bonded to almost any silicon-based substrate such as silica gel, flyash, glass, or soil. The bonding process involves hydrolysis of the silane to form a reactive silanol which then condenses on the surface of a substrate to form siloxane linkages. The siloxane bond is stable and imparts new properties to the

substrate. Since solidification processing systems rely on silicate chemistry to develop a solid mass, organosilane conditioning of additives could represent a useful technique for incorporating a sorbent into a solidification process. Of particular interest is evaluation of the toxic metal immobilization properties of sorbents when used in conjunction with solidification processing to treat hazardous waste.

Tests for Determining Process Effectiveness

Adsorption isotherms

14. Adsorption isotherms are routinely used to compare the relative ability of different sorbents to adsorb contaminants (Metcalf and Eddy, Inc. 1979). In an isotherm test the amount of contaminant removed is determined as a function of the aqueous concentration at a constant temperature. The resulting set of data is called an adsorption isotherm. In 1918 Langmuir suggested the following equation to model adsorption processes:

$$dC/dt = -K_1C(Q - q) + K_2q \quad (1)$$

where

C = concentration of contaminant in the aqueous phase, M_c/L^3

t = time

K_1 = Langmuir rate constant for adsorption, $M_s/M_c T$

Q = ultimate monolayer capacity of the sorbent, M_c/M_s

q = concentration of contaminant in the adsorbed phase, M_c/M_s

K_2 = rate constant for desorption, $M_s/(L^3 T)$

M_c = mass of contaminant

M_s = mass of sorbent

Although Langmuir modeled a gas-solid adsorption process, the Langmuir equation has been widely applied to aqueous-solid phase adsorption processes.

15. As indicated above, isotherm tests are equilibrium tests; that is, the contaminant flux from the aqueous phase into the solid phase is equal to the contaminant flux from the solid phase into the aqueous phase. At equilibrium $dC/dt = 0$, so that Equation 1 becomes

$$K_1 C(Q - q) = K_2 q$$

and after rearranging

$$q = K_d QC / (1 + K_d C) \quad (2)$$

where $K_d = K_1/K_2$ is the Langmuir distribution coefficient, L^3/M . When isotherm tests are run, a table of aqueous phase concentrations C and corresponding sorbent phase concentrations q can be prepared. When these data are plotted, a curve such as that shown in Figure 1 results. The curve

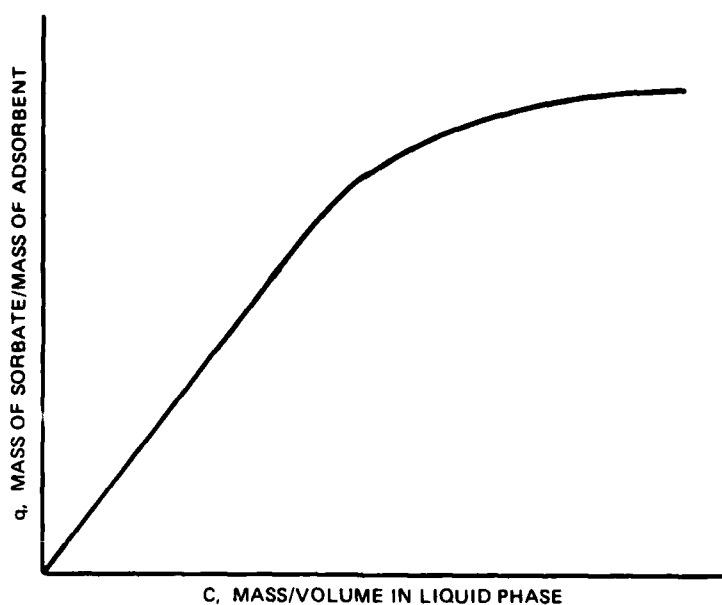


Figure 1. Typical adsorption isotherm

of adsorbed contaminant q versus aqueous phase concentration C asymptotically approaches some limiting value as C becomes large. This limit represents the ultimate capacity Q of the sorbent. Thus, the amount of contaminant adsorbed can be expressed as a function of the aqueous phase concentration and the ultimate capacity Q of the sorbent (Equation 2). Equation 2 can be rearranged into the linear form given below:

$$C/q = 1/(QK_d) + C/Q \quad (3)$$

The coefficients $1/(QK_d)$ and $1/Q$ can be determined by fitting experimental

data to Equation 3 by the method of least squares, from which Q and K_d are easily determined. The Langmuir distribution coefficient K_d is a measure of the affinity of the contaminant for one phase or the other. It is dependent on several factors such as pH, ionic strength, competition with other adsorbates, and surface area of the sorbate. As K_d becomes large, more and more of the contaminant resides, at equilibrium, in the sorbed phase. The distribution coefficient can also be interpreted as a measure of the irreversibility of the adsorption process. The larger K_d the smaller the desorption rate constant K_2 relative to the adsorption rate constant K_1 . When K_2 approaches zero, the desorption term in Equation 2 disappears, and there is no partitioning of the contaminant between aqueous and sorbed phases. For $K_2 = 0$, all of the contaminant will be in the adsorbed phase (up to the limit Q) when the system reaches equilibrium.

Toxicity extraction procedure (EP)

16. The EP is part of EPA's official protocol for classifying hazardous waste. In the original development of the EP, an acidic leaching medium was chosen to simulate leaching in a sanitary landfill environment. For wastes that are within the purview of RCRA but that are not specifically listed as hazardous in 40 CFR 261, the EP test is used to determine if the waste is hazardous. If such a waste fails the EP criteria, then it is classified as a hazardous waste. Otherwise it is not. Passing the EP does not, however, make a listed waste nonhazardous. Nonhazardous status for a listed waste is obtained by petitioning the EPA Administrator for a determination of nonapplicability (delisting). Delisting petitions are reviewed on a case-by-case basis. EP leach data are often used to support a delisting petition.

Uniform leach procedure (ULP)

17. Malone, Jones, and Larson (1980) proposed the ULP as a practical, reproducible, and uniform procedure for directly comparing the leaching characteristics of different solidified waste products. The ULP is a modification of the International Atomic Energy Agency (IAEA) leach test, originally proposed by Hespe (IAEA 1971). The original IAEA and subsequent modifications, such as the test used by Moore, Godbee, and Kibbey (1976), differ from the standard EPA leaching tests in several ways. There are major differences in test designs and in the approaches taken to data interpretation. Leaching tests can be carried out assuming the leaching process is governed by equilibrium partitioning or by kinetic processes. Because contaminant transfer from

waste solids to leachate may take place under either set of conditions, tests for both may be necessary. IAEA tests are kinetic tests. The EPA EP test is neither a kinetic nor an equilibrium test. The IAEA uses mass-transport theory to interpret leach data. The EP is a criteria-comparison type test in which leachate contaminant concentrations are compared with a published set of concentration limits.

18. Various equations that model contaminant loss under leaching conditions equivalent to those of the ULP have been described by Godbee and Joy (1974), Moore, Godbee, and Kibbey (1976), and Godbee et al. (1980). These equations were derived by application of mass-transport theory to laboratory systems. The model equation recommended by Malone, Jones, and Larson (1980), Equation 4 below, is the simplest of the models developed by Godbee and co-workers. This equation models the rate of appearance of contaminant in the leachate as contaminant diffusion through the interstices of a porous, semi-infinite solid having uniform initial contaminant distribution. At the surface the contaminant is assumed to be removed (leached) more rapidly than it arrives so that the surface concentration = 0 for time > 0. This means that the internal diffusion process is not limited by transport across the solid/liquid interface nor by diffusion away from the surface and into the leaching medium. Convective transport by percolation of water through the solid is not considered.

$$(\Sigma a_n / A_o)(V/S) = 2(D_e / \pi)^{0.5} t^{0.5} \quad (4)$$

where

Σa_n = total contaminant mass lost over n leaching cycles, M

A_o = initial amount of contaminant in solid waste, M

V = volume of specimen, L^3

S = exposed surface area of specimen, L^2

D_e = effective diffusivity, L^2/T

t = elapsed time

When considering the use of Equation 4, it is important to realize that the development of Equation 4 carries restraints imposed by the initial and boundary conditions that are used to solve the diffusion equation from which Equation 4 is derived (Cote 1983). These constraints are discussed later in

this report in the section on extrapolation of laboratory leach data to the field situation (paragraphs 55-62).

Desorption isotherms

19. The test conditions of the ULP, while appropriate for obtaining information on the leachability of durable, solidified waste products that are not permeable, are not suitable for developing information on permeable waste materials. For materials that are not appropriate candidates for ULP testing, desorption isotherms can be used to provide fundamental information on solid-liquid interactions that control transfer processes. Desorption isotherms have been used to investigate interactions between ground water and contaminated soils and sediments (Houle and Long 1980; Issacson and Frick 1984; McCarty, Reinhard, and Rittmann 1981; O'Conner and Connolly 1980). If the sorption processes of adsorption and desorption have taken place under identical conditions, then the desorption of a contaminant back into the aqueous phase should proceed down the adsorption isotherm and follow it exactly. However, the conditions under which adsorption takes place are usually significantly different from those under which desorption isotherms are developed. If the sorption systems differ significantly in pH, ionic strength, and chemical activity, the desorption process will not simply be a reversal of the adsorption process.

20. Jaffe and Ferrara (1983) suggested the following simple mass action desorption model:

$$dC/dt = -K_1' C + K_2 q \quad (5)$$

For steady-state conditions $dC/dt = 0$, and Equation 5 becomes Equation 6 below:

$$q = K_d' C \quad (6)$$

where

$$\begin{aligned} K_1' &= \text{rate constant for adsorption, } T^{-1} \\ K_2 &= \text{rate constant for desorption, } M_s / (L^3 T) \\ K_d' &= K_1 / K_2 \end{aligned}$$

Equation 6 describes the relationship between sorbed and aqueous phase concentration at equilibrium by a simple distribution coefficient K_d' . A typical desorption isotherm is shown in Figure 2. Each value of contaminant loading in the solid phase q supports a unique aqueous phase concentration C that at equilibrium is directly proportional to q by the distribution coefficient K_d' . This information can be used in a solute-transport model to simulate sorption processes in the field situation (Grove and Stollenwerk 1984).

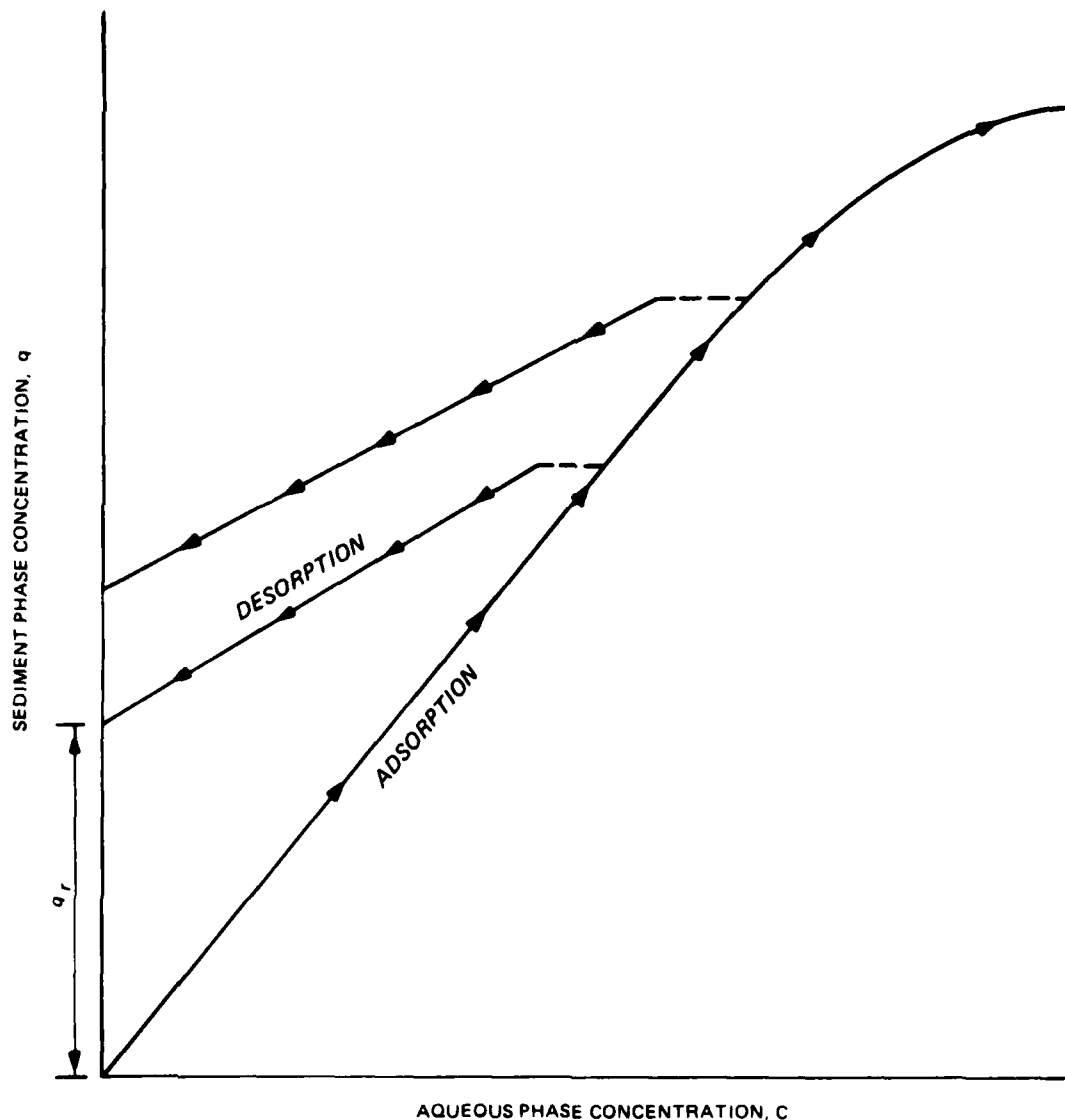


Figure 2. Typical desorption isotherm

PART III: MATERIALS AND METHODS

Basin F Liquid

21. The data presented in this report describe results from tests conducted on liquid residue collected from Basin F at Rocky Mountain Arsenal (RMA) in February 1983. Basin F is a hazardous waste lagoon that has been identified as a source of contamination requiring control and elimination. The liquid in Basin F impacts the environment through migration of contaminants to ground water beneath the basin, by volatilization of contaminants to the air, and through direct contact with wildlife. One treatment/disposal option under consideration involves solidification of residual liquids and sludges followed by secure landfilling of the solidified waste (Myers and Thompson 1983).

22. Basin F liquid is a concentrated brine that contains significant amounts of organic materials. Depending on precipitation and evaporation, the liquid ranges from 5.2 to 7.9 percent by weight total organic carbon, 9.9 to 13.7 percent by weight chloride, 2.5 to 3.2 percent by weight ammonia nitrogen, and 0.31 to 0.53 percent by weight copper. Lesser amounts of other contaminants such as cadmium, arsenic, aldrin, and mercury are present.

Sorbent Preparation and Testing

Preparation

23. Soil and flyash sorbents with and without silane conditioning were prepared. The soil was obtained from near the intersection of "E" Street and 9th Avenue at RMA. It was sieved through 6.35-cm wire mesh, dried at 40° C, and ground with a mortar and pestle. The particle-size distribution of the soil is shown in Figure 3. The flyash was obtained from the Cherokee Power Plant, Denver Public Service Company. The specific gravity of the ash was 2.07, and it contained 4.7 percent lime by weight as CaO. The moisture content was 0.2 percent. A pozzolan report by the Cement and Pozzolan Unit, Structures Laboratory, US Army Engineer Waterways Experiment Station (WES) is presented in Appendix A.

24. The preparation of silane-conditioned sorbents involves the bonding of N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane to a substrate. This

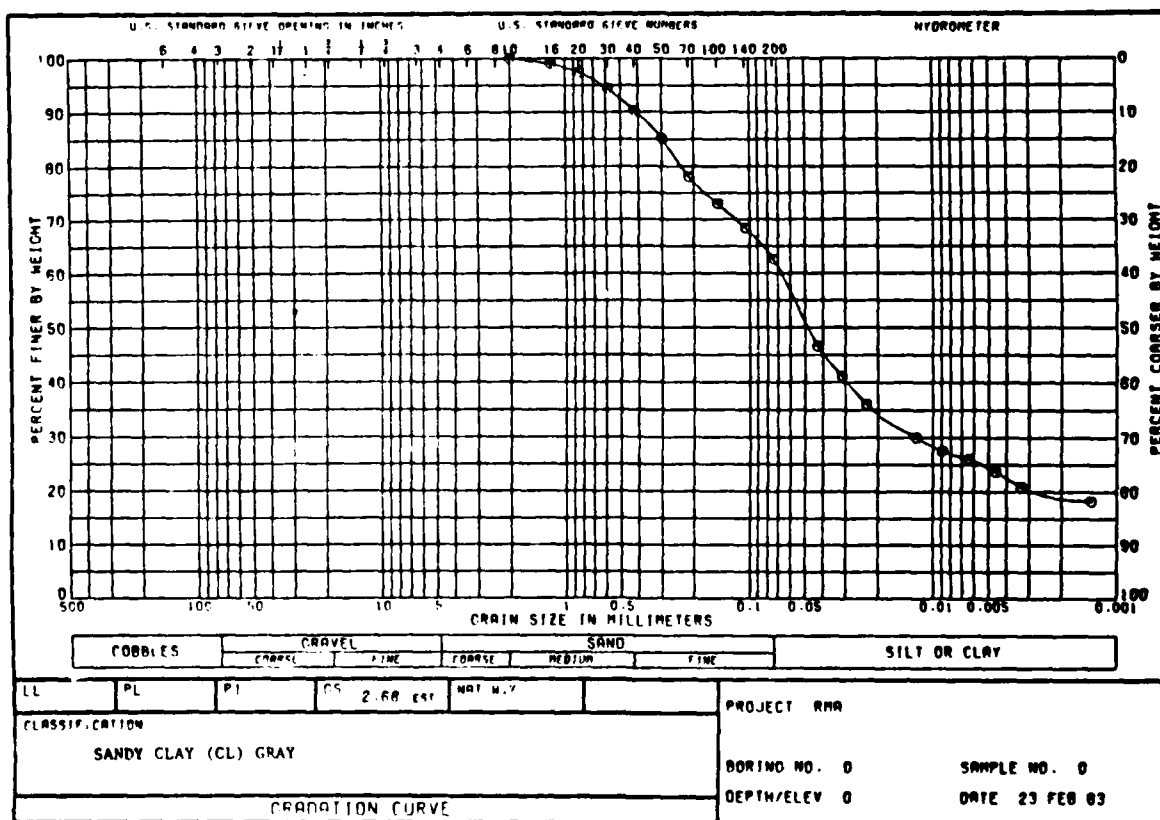


Figure 3. Grain-size distribution of RMA soil used as an adsorbent

organosilane is manufactured by Dow Chemical Company as Dow Z-6020. The Dow Z-6020 used in this study was obtained from SCM Speciality Chemicals, Gainesville, Fla. Dow Z-6020 is a chelating agent that chelates copper, chromium, zinc, lead, and cadmium (Leyden and Luttrell 1975). Several sorbent batches were prepared using different amounts of silane with either soil or flyash as the substrate in order to determine which was the better substrate, and to determine the most effective dosage of silane. Two silane-substrate bonding procedures were used in order to investigate the effect that various sorbent preparation procedures have on adsorption characteristics. The procedure adapted from Leyden and Luttrell (1975) consisted of the following steps:

- a. Two aqueous silane solutions (1.0 and 10.0 percent by volume) were prepared by adding silane to deionized-distilled water with stirring. The solutions were acidified to pH 5 to 6 by adding reagent grade glacial acetic acid. The pH was checked with pH paper. Plastic labware was used to avoid reaction with glass.
- b. Flyash or soil substrate was contacted with the aqueous silane solutions on a mechanical shaker for 30 min at liquid-to-solid

ratios of 1 ml aqueous silane solution to 1 g of substrate and 1.5 ml of aqueous silane to 1 g of substrate.

- c. The mixture was reacted at 70° C in a vented oven for 24 hr. In one bonding procedure the loss of water was controlled so that the mixture was not allowed to completely dry. In another the mixture was dried at 70° C for 48 hr.
- d. The sorbent preparations that were allowed to dry were washed with water to remove excess silane and then dried at 40° C.
- e. The wet sorbent preparations were washed with water to remove excess silane and then air dried.

25. Several sorbents from the two substrates were prepared using wet and dry bonding conditions. Three organosilane dosages ranging over an order of magnitude were used. Table 1 is a summary of the sorbents that were prepared, the organosilane dosages used in each preparation, and the bonding procedures employed. Duplicate batches of selected soil/silane sorbent preparations were made in order to replicate some of the adsorption isotherm tests.

Adsorption isotherms

26. Adsorption isotherms were run in order to determine the ultimate capacity and equilibrium constants of the various sorbents for copper. One gram of sorbent was contacted on a mechanical shaker for 24 hr with 100 ml of various dilutions of Basin F liquid. Each mixture was then filtered and analyzed for soluble copper. Six dilutions of Basin F liquid were used in each isotherm test as follows: 1,000/1, 100/1, 50/1, 10/1, 5/1, and 1/1 (no dilution). Blanks consisting of sorbent and deionized water were run with each adsorption isotherm test. Liquid-solid separation was accomplished by filtration using Gelman No. 61631 glass fiber filters. Adsorption isotherms were developed for soil, soil with silane, flyash, and flyash with silane sorbents.

27. A kinetic adsorption test was run in order to determine if the 24-hr contact time was sufficient for the adsorption isotherm tests to reach steady-state conditions. The test was run on a 10/1 dilution of Basin F liquid using 100 ml of dilute waste with 1 g of a soil/silane sorbent. Aqueous copper concentration was monitored for various contact times ranging from 1 hr to 24 hr. Liquid-solid separation was accomplished by filtration using Gelman No. 61631 glass fiber filters.

Table 1
Sorbent Preparations

<u>Sorbent</u>	<u>Substrate</u>	<u>Silane Dosage</u>	<u>Bonding Procedure</u>
S-A&B*	Soil	None	NA**
F	Flyash	None	NA
S/S-1.0d	Soil	1.0 ml of 1% aqueous silane to 1 g substrate	Taken to dryness at 70° C
F/S-1.0d	Flyash	1.0 ml of 1% aqueous silane to 1 g substrate	Taken to dryness at 70° C
S/S-1.5d-A&B	Soil	1.5 ml of 1% aqueous silane to 1 g substrate	Taken to dryness at 70° C
S/S-1.5w	Soil	1.5 ml of 1% aqueous silane to 1 g substrate	Simmered at 70° C
F/S-1.5d	Flyash	1.5 ml of 1% aqueous silane to 1 g substrate	Taken to dryness at 70° C
S/S-15d-A&B	Soil	1.5 ml of 10% aqueous silane to 1 g substrate	Taken to dryness at 70° C
S/S-15w	Soil	1.5 ml of 10% aqueous silane to 1 g substrate	Simmered at 70° C
F/S-15d	Flyash	1.5 ml of 10% aqueous silane to 1 g substrate	Taken to dryness at 70° C

* A&B = Duplicate batches prepared.

** NA = Not applicable.

Waste Solidification and Testing

Solidification

28. The feasibility of solidification processing of Basin F liquid has been investigated in bench scale studies (Myers and Thompson 1983). Physical testing of products from different solidification processes showed that Basin F liquid can be converted to solid form. Chemical leach testing, however, showed that copper and other metals were mobile and could be leached from the solidified waste.

29. Of the various processes investigated, one was a generic process for which the process formulation was exactly known, while the remainder were commercial processes with proprietary formulations. The generic process involved the use of three primary additives: soil from RMA, flyash from a local power plant, and lime as calcium hydroxide. This process was chosen for investigation in this study because it included two materials with sorbent potential (soil and flyash) and because a workable formulation was known. Other additives have been used with the soil/flyash/lime process to sequester ammonia off-gassing (Myers and Thompson 1984). Several soil/flyash/lime formulations were used to solidify Basin F liquid for leach testing as follows: (a) a formulation using 1:1:1:1 weight ratios of soil/flyash/lime/Basin F liquid with and without organosilane conditioning of the soil, and (b) a formulation using 0.7:0.7:0.7:1 weight ratios of soil/flyash/lime/Basin F liquid with and without silane conditioning of the soil and ammonia sequestering reagents in stoichiometric ratios of 0.0, 1.15, and 1.5. Table 2 provides a summary of the process formulations used in this study.

30. Because sequestering reagents assist in the development of a hardened product, the additive-to-waste ratios were reduced in formulations that included the use of sequestering reagents. The stoichiometric ratio is the ratio of the amount of sequestering reagents used to the amount required on the basis of chemical stoichiometry. The two sequestering reagents used were magnesium sulfate and concentrated phosphoric acid. On the basis of stoichiometry, 1 g-mole of magnesium sulfate and 1 g-mole of phosphate are required for each gram-mole of ammonia nitrogen. These reagents form an ammonium complex that is essentially insoluble. The effectiveness of chemically

Table 2
Process Formulations Used in This Study

<u>Additives</u>	<u>Lime/Flyash/Soil/Waste Weight Ratio</u>
Lime, flyash, soil	0.7/0.7/0.7/1 1/1/1/1
Lime, flyash, 1% silane- conditioned soil	0.7/0.7/0.7/1 1/1/1/1
Lime, flyash, 10% silane- conditioned soil	1/1/1/1
Ammonia sequestering reagents (SR) (SR = 1.15), lime, flyash, soil	0.7/0.7/0.7/1
Ammonia sequestering reagents (SR = 1.15), lime, flyash, 1% silane-conditioned soil	0.7/0.7/0.7/1
Ammonia sequestering reagents (SR = 1.50), lime, flyash, soil	0.7/0.7/0.7/1
Ammonia sequestering reagents (SR = 1.50), lime, flyash, 10% silane-conditioned soil	0.7/0.7/0.7/1

sequestering ammonia off-gassing using these reagents has been described in a patent disclosure by Myers and Thompson.*

31. Sequestering reagents were added to Basin F liquid prior to the addition of the solidification reagents. The solidification additives were mixed with Basin F liquid in a Hobart C-100 mixer in the order indicated in the formulation. The soil and liquid were mixed for 30 min. Mixing times for the flyash and lime were 3 to 5 min each. After mixing, the freshly prepared solidified waste was allowed to cure for 30 min. It was then compacted in standard Corps of Engineers (CE) compaction molds (McIver and Hale 1970).

32. Table 3 shows the experimental matrix of leaching tests and test materials. EP's and ULP's were run on solidified Basin F liquid processed using additives-to-Basin-F ratios of 0.7/0.7/0.7/1 and 1/1/1/1, with and

* T. E. Myers and D. W. Thompson. Letter of request for consideration of patent application, 29 September 1984.

Table 3
Experimental Matrix for Leaching Tests*

Formulation**	Waste Solidification		Leaching Test			
	SR	Sorbent†	EP	DI	ULP	KD
0.7/0.7/0.7/1	0.00	Soil	X			
0.7/0.7/0.7/1	0.00	S/S-1.5w	X			
0.7/0.7/0.7/1	1.15	Soil	X		X	
0.7/0.7/0.7/1	1.15	S/S-1.5d	X		X	
0.7/0.7/0.7/1	1.50	Soil	X			
0.7/0.7/0.7/1	1.50	S/S-15d	X			
1/1/1/1	0.00	Soil	X	X	X	X
1/1/1/1	0.00	S/S-1.5w	X	X	X	X
1/1/1/1	0.00	S/S-15w	X	X		X

* SR = Stoichiometric ratio, the amount of sequestering reagents added divided by the amount needed on the basis of stoichiometry. EP = EPA toxicity extraction procedure. DI = Desorption isotherms. ULP = Uniform leach procedure. KD = Kinetic desorption test.

** Lime/flyash/soil/Basin F liquid.

† See Table 1.

without silane conditioning of the soil and with and without ammonia gas sequestering reagents. Desorption isotherm tests and kinetic desorption tests were run on solidified Basin F liquid processed using 1/1/1/1 weight ratios of additives to Basin F liquid, with and without organosilane conditioning of the soil additive.

Testing

33. Toxic extraction procedure. The EPA toxic extraction procedure was run on solidified waste samples according to the procedure specified in 40 CFR 261 (USEPA 1980). This test consists of contacting dilute acetic acid with approximately 100 g of solidified waste in a liquid-to-solids ratio that varies between 16/1 to 20/1 depending on waste alkalinity. The duration of the test varies from 24 to 28 hr, also depending on waste alkalinity. Liquid-solid separation was accomplished by filtration using Millipore HAWP 142-50 membrane filters.

34. Desorption isotherms. Desorption isotherms were developed by contacting solidified waste samples with deionized-distilled water on a mechanical shaker for 24 hr using five liquid-to-solid ratios: 50 ml/5 g,

50 ml/2 g, 50 ml/1 g, 100 ml/1 g, and 100 ml/0.5 g. The mixtures were filtered and analyzed for soluble copper. Blanks consisting of deionized-distilled water were included in each set. Liquid-solid separation was accomplished by filtration using Gelman No. 61631 glass fiber filters. Kinetic desorption tests were run on two solidification products in order to determine if the 24-hr contact time was sufficient for the desorption isotherm tests to reach steady-state conditions. One solidification process used soil without silane as an additive and the other used a soil/silane additive. A liquid-to-solids ratio of 50 ml deionized-distilled water to 1 g of solidified waste was used. The aqueous phase copper concentration was monitored with time by contacting deionized water and solidified waste for times ranging from less than 1 hr to 24 hr. Liquid-solid separation was accomplished by filtration using Gelman No. 61631 glass fiber filters.

35. Uniform leach procedure. The uniform leach procedure recommended by Malone, Jones, and Larson (1980) was run on solidified waste samples. In this test a molded specimen of solidified waste of known volume and weight was submerged in a known volume of water and allowed to leach. At the end of each 24-hr leaching cycle, the water was removed, analyzed for copper, and replaced with a fresh quantity of water. Waste specimens were prepared by compacting freshly prepared solidified waste in standard CE compaction molds. The standard CE compaction mold is a cylinder with a 10.2-cm inside diameter and 11.7 cm in height. The volume of the mold is 943 cm^3 . Each molded cylinder of solidified waste was leached in a plastic bucket with 13.25 l of reverse-osmosis treated water. The experimental setup of the ULP is shown in Figure 4. Each solidified waste specimen was allowed to cure for at least 7 days before the ULP was initiated. Specimen weight was taken immediately prior to testing. Liquid-solid separation was accomplished by filtration using Gelman No. 61631 glass fiber filters.

Chemical Analysis

36. Isotherm and leach test samples were analyzed for copper on a directly coupled argon plasma emission spectrophotometer by the Analytical Laboratory Group, Environmental Laboratory, WES. Copper was selected for investigation because it is present in Basin F liquid in high concentrations (4,040 mg/l for the material used in this study), analysis for copper is

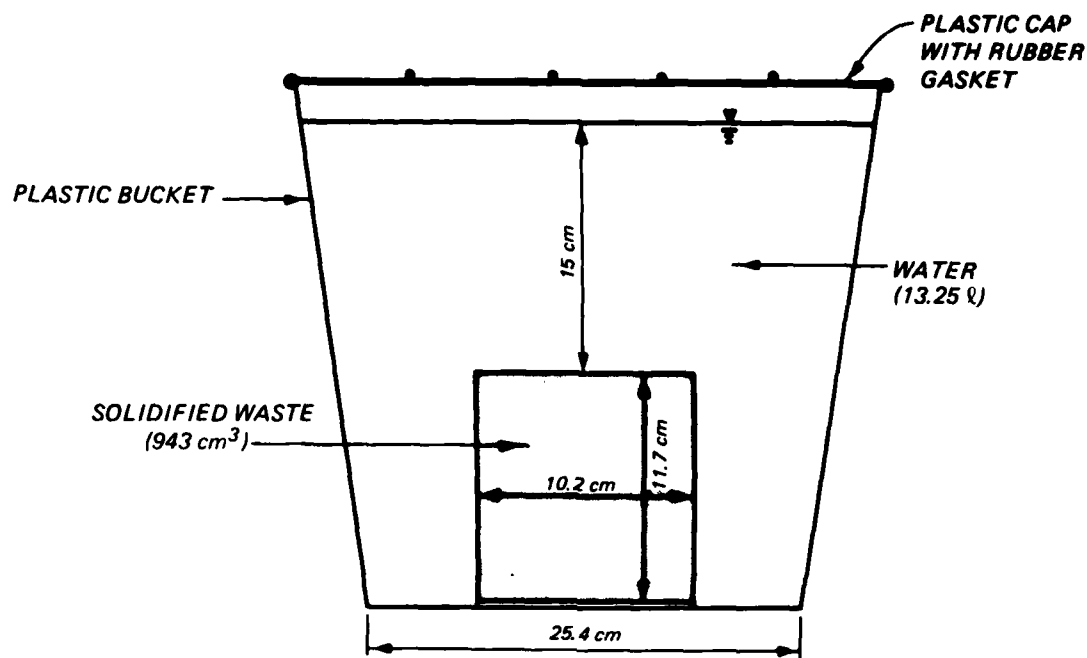


Figure 4. Schematic of ULP test setup

relatively easy and reliable, and copper adsorption can be used as an indicator of overall metal sorption processes.

37. Copper is a suitable model for investigation of metal sorption processes because its chemical properties are related to those of several toxic metals. Copper, cadmium, zinc, gold, silver, and mercury are grouped together in the periodic chart as Group IB and IIB elements because they have similar electron shells and share certain chemical properties. The adsorption characteristics of copper have been reported to be similar to those of cadmium, lead, and chromium by Leyden and Luttrell (1975).

PART IV: RESULTS AND DISCUSSION

Sorbent Testing

Kinetic adsorption tests

38. Kinetic adsorption tests were run on soil and one soil/silane sorbent (S/S-1.5d) in order to determine the time required for the sorption systems to reach steady-state. Adsorption kinetics were investigated by observing the change in soluble copper concentration with time. The data for the selected sorbent are presented in Table 4. These data, which are typical of the kinetic adsorption data, indicate that equilibrium is established after about 6 hr. Thus, the 24-hr contact time used in the adsorption isotherms discussed below is sufficient for the aqueous phase contaminant concentrations to stabilize at steady-state values.

Adsorption isotherms

39. The adsorption isotherm data obtained in this study are presented in Table 5. Table 5 lists the dilution of BF liquid for each adsorption point, aqueous phase concentrations of copper C , adsorbed phase concentrations of copper q , sorbent ultimate capacity for copper Q , and the distribution coefficient K_d for the sorbents investigated in this study. The values of Q and K_d were obtained by least squares fitting of data to Equation 3.

40. Figure 5 presents selected isotherm curves from Table 5. The notation used in Table 5 and Figure 5 relates to the sorbents described in Table 1. For example, the sorbent denoted as "S/S-1.5d" was the soil/silane sorbent prepared by taking to dryness a mixture of 1.5 ml of 10% aqueous silane per gram of soil. Similarly the sorbent denoted as "S/S-1.5w" was the sorbent prepared with a mixture of 1.5 ml of 1 percent aqueous silane per gram of soil without being taken to dryness. "S" designates soil without silane, and "F" designates flyash without silane. All of the flyash/silane sorbent preparations were prepared by taking the flyash/silane mixture to complete dryness at 70° C.

41. The isotherm data in Table 5 and the curves in Figure 5 show that conditioning of the soil with silane at the right dosage and under the right conditions can enhance the ultimate adsorption capacity Q and can reduce the reversibility of the adsorption process. The ultimate adsorption capacities of the various sorbents were ordered as follows: S/S-1.5d > S/S-1.5w >

Table 4
Kinetic Adsorption Results for S/S-1.5d*

Time hr	Aqueous Phase Copper Concentration	Average Concentration mg/l
	mg/l	
1	335 334	334.5
2	334 341	337.5
4	336 328	332
6	323 327	325
8	331 323	327
12	317 330	323.5
24	329 329	329

* S/S-1.5d is the sorbent prepared with a mixture of 1.5 ml of 1-percent aqueous silane per gram of soil, bonded by drying at 70° C.

F/S-1.5d > S/S-1.5d > S/S-1.0d > F/S-1.5d > S > S/S-1.5w > F > F/S-1.0. On the basis of ultimate adsorption capacities, the organosilane-conditioned sorbents were superior to the unconditioned sorbents, and the soil-based sorbents were superior to the flyash-based sorbents. The range of observed ultimate adsorption capacity is probably not as large as it would have been had standard copper solutions been used in the adsorption isotherm tests. In the high strength dilutions of Basin F liquid, competing ions probably reduced the number of adsorption sites available for copper adsorption. There are other effects related to using undiluted Basin F liquid in adsorption isotherm tests that can obscure differences in ultimate adsorption capacities. These effects include nucleation (growth of salt crystals on sorbent particles) that blocks access to the adsorption sites, deactivation by reaction of organic substances in Basin F liquid with the organosilane, and combinations of these. As a

Table 5
Adsorption Isotherm Data

Sorbent	BF Dilution	C mg/l	q mg/l	C/q g/l	K _d l/mg	Q mg/g	r*
Soil**	1,000	0.719	0.3181	2.260296			
	100	19.6	1.94	10.10309			
	50	48.4	2.96	16.35135	0.0229	6.6	0.9999
	10	334.5	5.55	60.27027			
	5	717.5	6.25	114.8			
	1	3,835	6.5	590			
S/S-1.0d†	1,000	0.34	0.37	0.9189189			
	100	17.9	2.25	7.955556			
	50	48	3.28	14.63415	0.0191	8.1	0.9999
	10	336	6.8	49.41176			
	5	735	7.3	100.6849			
	1	3,960	8	495			
S/S-1.5d**	1,000	0.183	0.3857	0.4744620			
	100	15.15	2.525	6			
	50	43.2	3.76	11.48936	0.0308	9.6	0.9997
	10	325	7.9	41.13924			
	5	708	10	70.8			
	1	3,945	9.5	415.2632			
S/S-1.5w†	1,000	0.461	0.329	1.401216			
	100	19.4	1.82	10.65934			
	50	44.4	3.08	14.41558	0.0117	6.1	0.9979
	10	329	4.7	70			
	5	708	4.4	160.9091			
	1	3,700	6	616.6667			

(Continued)

- * r = Coefficient of variation.
 ** Average of two tests.
 † Single test.

(Sheet 1 of 3)

Table 5 (Continued)

Sorbent	BF Dilution	C mg/l	q mg/l	C/q g/l	K _d l/mg	Q mg/g	r
S/S-15d**	1,000	0.065	0.795	0.0817610			
	100	6.44	3.396	1.896349			
	50	23.3	5.75	4.052174	0.0265	15.2	0.9999
	10	281.5	12.25	22.97959			
	5	667	14.1	47.30496			
	1	3,887.5	15.25	254.9180			
S/S-15w†	1,000	0.197	0.3693	0.5334416			
	100	12.7	2.62	4.847328			
	50	39.1	3.87	10.10336	0.00829	11.2	0.9966
	10	319	7	45.57143			
	5	702	7.6	92.36842			
	1	3,780	11	343.6364			
Flyash†	1,000	0.432	0.3608	1.197339			
	100	20.2	2.02	10			
	50	56.9	2.39	23.80753	-0.03	3.4	0.9984
	10	367	3.7	99.18919			
	5	761	4.7	161.9149			
	1	4,006	3.4	1178.235			
F/S-1.0d†	1,000	0.522	0.3518	1.483798			
	100	21.8	1.86	11.72043			
	50	56.4	2.44	23.11475	-0.0201	3.1	0.9962
	10	373	3.1	120.3226			
	5	753	5.5	136.9091			
	1	4,009	3.1	1293.226			

(Continued)

** Average of two tests.

† Single test.

(Sheet 2 of 3)

Table 5 (Concluded)

Sorbent	BF Dilution	C mg/l	q mg/l	C/q g/l	K _d l/mg	Q mg/g	r
F/S-1.5d†	1,000	1.67	0.237	7.046414			
	100	32.8	0.76	43.15789			
	50	70.9	0.99	71.61616	0.0015	10.4	0.9141
	10	385	1.9	202.6316			
	5	775	3.3	234.8485			
	1	3,950	9	438.8889			
F/S-15d†	1,000	3.72	0.032	116.25			
	100	9.49	3.091	3.070204			
	50	32.7	4.81	6.798337	0.0054	7.2	0.9783
	10	329	7.5	43.86667			
	5	739	6.9	107.1014			
	1	3,972	6.8	584.1176			

† Single test.

(Sheet 3 of 3)

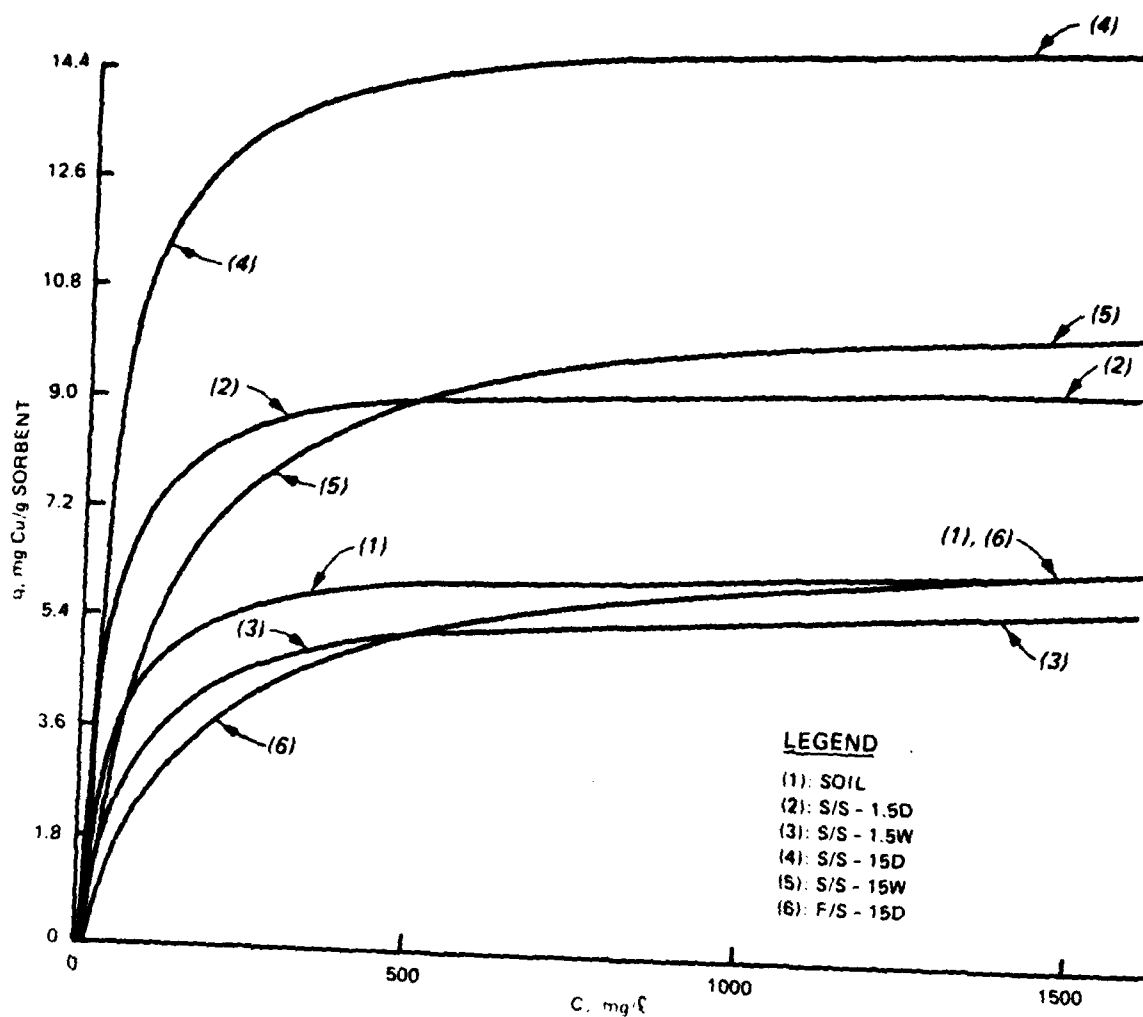


Figure 5. Selected adsorption isotherm curves

result, the ultimate adsorption capacities presented in Table 5 are probably better used for qualitative rather than quantitative comparisons.

42. The isotherm data show that conditioning the soil with organosilane can reduce the reversibility of the adsorption process. Reduced reversibility is indicated by an increase in the distribution coefficient and by an increase in slope of the linear portion of the curves in Figure 5. When K_d is large the desorption rate coefficient is small in relation to the adsorption rate coefficient. In terms of leaching potential, the higher the distribution coefficient K_d , the lower the aqueous concentration C that a given sorbent loading q will support. Hence, the less reversible the adsorption process,

the less leachable the contaminant. The Langmuir distribution coefficients were ordered as follows: $S/S-1.5d > S/S-15d > S > S/S-1.0d > S/S-1.5w > S/S-15w > F/S-15 > F/S-1.5 > F/S-1.0 > F$. The highest distribution coefficients were obtained with organosilane-conditioned soil. This is probably due to a chemisorption component in the soil/silane adsorption process that is irreversible or only slightly reversible.

43. The best copper sorbent investigated in this study, as indicated by the isotherms shown in Figure 5, was S/S-15d. Soil was generally less effective than the soil/silane sorbents especially when the soil/silane mixture was completely dried during sorbent preparation. The poor performance of the flyash preparations is probably due to physical/chemical properties of the flyash that relate to the ash generation process in the boiler flue gas. Flyash from coal-fired power plants is an almost entirely inorganic product having a glassy nature. Consequently, flyash by itself has little absorbency. The data in Table 5 also indicate that the flyash used in this study was a poor substrate for organosilane bonding.

44. The adsorption isotherm data show that the soil is more than just a filler, even without organosilane conditioning. The adsorption capability of soils for metals is well known (Fuller et al. 1980; Griffin et al. 1976; Jenne 1968; Korte et al. 1975, 1976). The data collected in this study show that copper is adsorbed by the soil and not simply entrapped in the solid matrix provided by solidification. This effect was observed in an earlier study where the soil/flyash/lime process leached smaller amounts of copper and other metals than did the other processes that were investigated (Myers and Thompson 1983).

45. The isotherm data also indicate that the soil/organosilane bonding procedures as well as the organosilane dosage affect sorbent performance. The sorbent produced using the complete drying process was superior to that produced using the wet process. One possible explanation for this observation relates to the collision frequency between the organosilane molecules and active (OH-) sites on the soil surface. The reaction of silane with a substrate involves hydrolysis of the methoxy groups, polymerization by condensation, hydrogen bonding between the condensed silane polymer, and finally formation of a silicon-oxygen bond (siloxane) between the substrate and the organosilane (Arkles 1977). This reaction sequence is shown in Figure 6. Apparently the final step is not accomplished until condensed organosilane

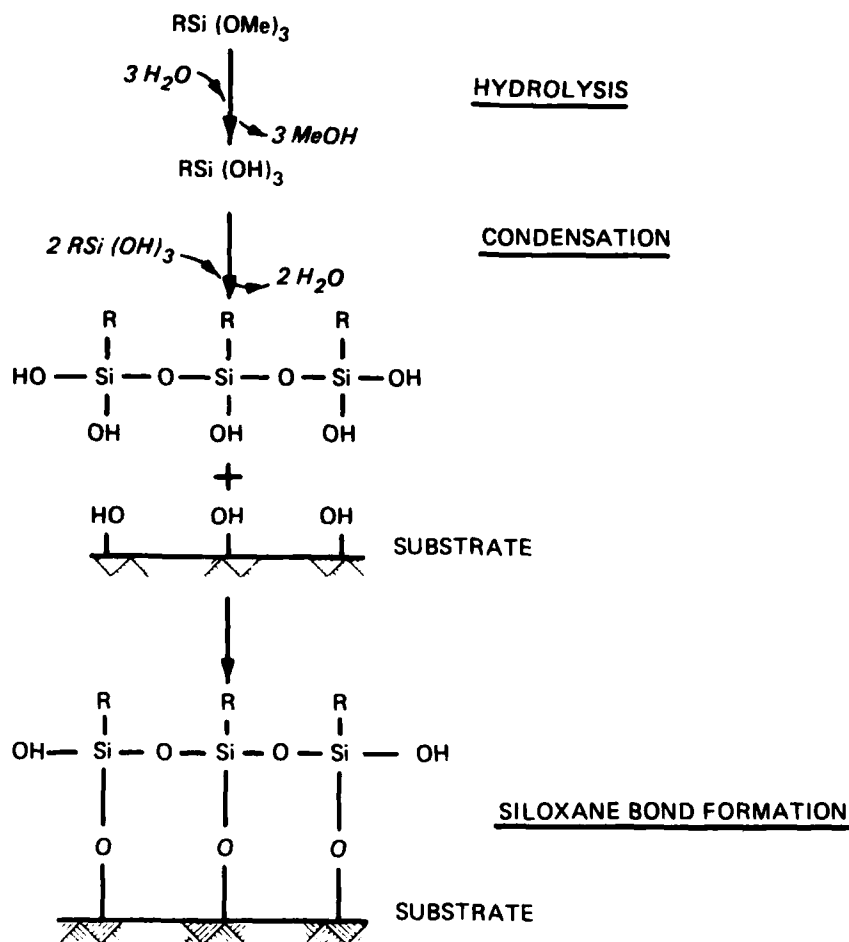


Figure 6. Organosilane bonding to a substrate

polymer and active sites on the soil surface are forced into a high collision probability by taking the mixture to dryness. The data indicate that it is probably necessary to take aqueous silane/substrate mixtures to dryness before the sorbent is washed of excess organosilane in order to bond the organosilane to the substrate. This requirement impacts the selection and operation of full-scale equipment for mixing and reacting organosilane with a substrate, and will affect the cost-effectiveness of organosilane usage in full-scale solidification projects.

Solidified Waste Leach Testing

Toxicity extraction procedure

46. The EP data are presented in Table 6. EP's were run on Basin F

liquid solidified with and without ammonia gas sequestering reagents and on Basin F liquid solidified with and without organosilane conditioning of the soil additive. Two stoichiometric ratios of sequestering reagents and two organosilane concentrations were used. Copper leach data normalized with respect to the mass of Basin F liquid processed are also presented. The normalized EP leachable concentrations are expressed as copper concentration (milligrams per litre) leached per 100 g of Basin F liquid processed. An important requirement of comparative testing is reproducibility. The reproducibility of the duplicates in Table 6 is very good in most instances. In the one or two instances where the reproducibility is not good, it does not obscure the differences in EP leachability.

47. Organosilane conditioning of the soil additive lowered the EP leachability of copper. This is shown in Figure 7a. The improved adsorption (possibly chemisorption) characteristics produced by organosilane conditioning of the soil on copper leachability have been discussed previously. The reductions in copper leachability indicated in Figure 7a are for soil/organosilane substrates prepared without taking the soil/organosilane mixture to complete dryness before washing. Had the soil/organosilane mixtures been taken to dryness during sorbent preparation, the adsorption isotherm data indicate that the reduction in copper leachability would have been even greater.

48. The addition of ammonia sequestering reagents in the absence of organosilane conditioning of the soil lowered the EP leachability of copper. This is shown in Figure 7b. The use of sequestering reagents also has a positive effect on the physical strength of solidified Basin F liquid (Myers and Thompson 1984). A stoichiometric ratio for the sequestering reagents of 1.15 leached the least amount of copper. There are several factors that could be involved in the sequestering reagents' effect on copper leaching. These include entrapment of soluble copper salts in a stronger matrix and development of less soluble copper compounds, such as ammonium-copper complexes with phosphate and sulfate ions.

49. The combined effect of the sequestering reagents and organosilane conditioning of the soil was to increase the EP leachability of copper from solidified Basin F liquid. When the organosilane-conditioned soil and sequestering reagents were used in the same process formulation, the amount of copper leached was approximately the same or was slightly higher than that leached when unconditioned soil and sequestering reagents were used in the

Table 6
Copper EP Leach Data for
Solidified Basin F Liquid

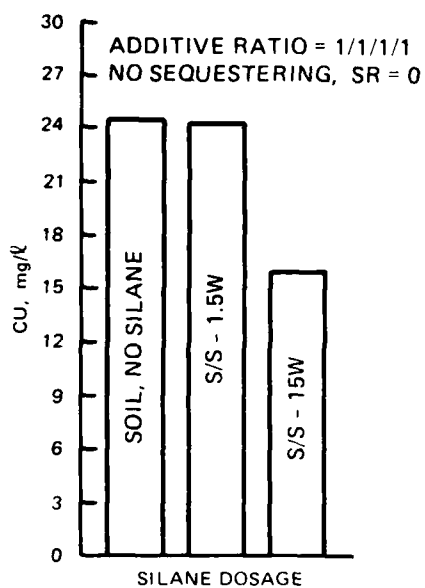
<u>Additive Ratio*</u>	<u>SR**</u>	<u>Sorbent†</u>	<u>EP Copper mg/l</u>	<u>Norm EP CU mg/l††</u>
0.7/0.7/0.7/1	0	S	8.25 3.81	18.7
0.7/0.7/0.7/1	1.15	S	1.01	3.86
0.7/0.7/0.7/1	1.5	S	3.47 3.45	14.1
0.7/0.7/0.7/1	0	S/S-1.5w	9.21 9.27	28.6
0.7/0.7/0.7/1	1.15	S/S-1.5d	1.33	5.09
0.7/0.7/0.7/1	1.5	S/S-15d	4.55 4.78	18.9
1/1/1/1	0	S	6.42 5.82	24.5
1/1/1/1	0	S/S-1.5w	6.04 6.09	24.3
1/1/1/1	0	S/S-15w	3.86 3.99 3.84	15.6

* Lime/Flyash/Soil/Basin F liquid.

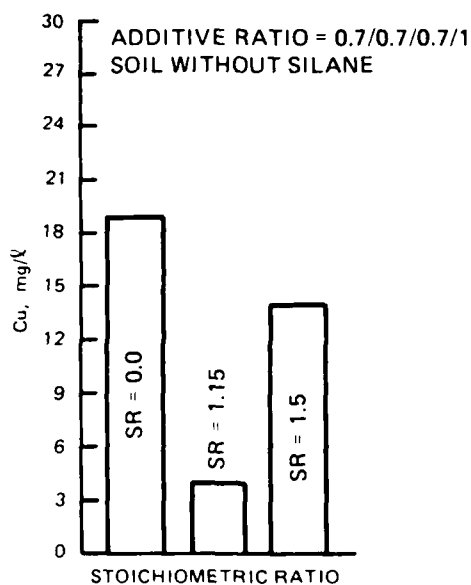
** SR = Stoichiometric ratio of ammonia sequestering reagents to ammonia present in Basin F liquid.

† See Table 1 for description of sorbents.

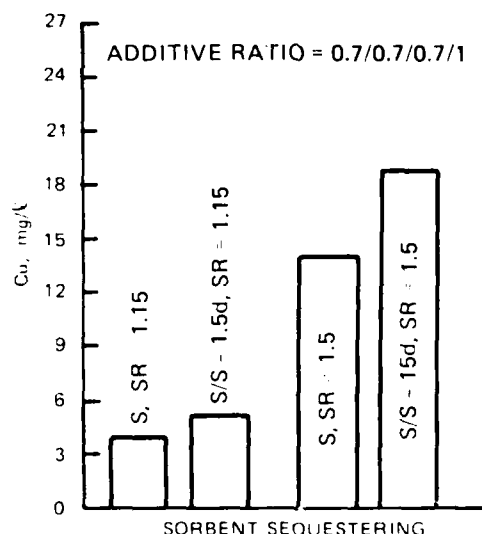
†† Norm EP CU = Copper concentrations in EP leachates normalized to 100 g Basin F liquid.



a. No sequestering, SR = 0



b. Soil without silane



c. Sequestering and soil with silane

Figure 7. EP leachable copper per 100 g Basin F liquid

process formulation. This is shown in Figure 7c. These data indicate that the sequestering reagents probably partially deactivate the adsorption of copper by organosilane bonded to the soil. A likely process by which this occurs is acid hydrolysis of the siloxane bond between the soil and the silicon atom of the organosilane molecule by one of the sequestering reagents, concentrated phosphoric acid. Both acid and base hydrolysis is possible (Leyden and Luttrell 1975). Acid hydrolysis by concentrated phosphoric acid could be avoided by using another phosphate source such as a phosphate salt. Base hydrolysis by the lime in the solidification process formulation is also a possibility.

Kinetic desorption test

50. The kinetics of desorption were investigated by observing the change in copper concentration in the liquid phase with time. Kinetic desorption tests were run on solidified Basin F liquid processed using 1/1/1/1 weight ratios of soil/flyash/lime/Basin F liquid with and without organosilane conditioning of the soil. The kinetic desorption data are presented in Table 7. These data indicate that equilibrium is approached after 24 hr, although perhaps not entirely reached. The reproducibility between duplicates is in some cases poor which makes a determination of equilibrium status difficult. Duplicates were not run for the S/S-15w sorbent. The 24-hr contact time used in the desorption isotherm tests discussed below was probably enough for the aqueous contaminant concentrations to reach an "apparent" equilibrium position. The fraction leached in 24 hr probably consisted of precipitated soluble salts and sorbed copper on the surfaces of the solidified waste. Slow bleeding of copper from the micropores of the particles to the surface probably accounts for the slow increase in copper concentrations after 24 hr of testing.

Desorption isotherms

51. Desorption isotherm tests were run on three types of solidified Basin F liquid. All three solidification process formulations used 1/1/1/1 weight ratios of soil/flyash/lime/Basin F liquid. In two of the formulations the soil was conditioned with organosilane, and in one the soil was not conditioned. The desorption isotherm data are presented in Table 8. Sorbed versus aqueous phase concentrations are plotted in Figure 8. The data plotted in Figure 8 fit the linear model of q versus C presented in Equation 6. The desorption isotherms show that sorbent-assisted solidification using a S/S-15w

Table 7
Time-Dependent Desorption of Copper
From Solidified Basin F Liquid*

Time hr	Aqueous Copper Concentration, mg/l					
	Soil	Ave.	S/S-1.5w	Ave.	S/S-15w	Ave.
0.5	ND**		ND		1.53 1.65	1.59
1	1.42 1.47	1.445	4.02 2.24	3.13	1.66 1.68	1.67
2	1.06 3.08	2.07	1.78 1.54	1.66	1.8 1.8	1.80
4	2.77 3.37	2.92	3.87 2.81	3.34	2.08 2.05	2.065
8	1.11 3.1	2.105	1.54 1.38	1.46		
14	1.05 1.18	1.084	3.88 1.5	2.69		
24	0.705 1.36	1.0325	2.5 2.23	2.365	1.98 2.02	2.00
43	1.55 1.48	1.515	2.53 2.23	2.38		
95	1.2 1.34	1.27	2.07 1.78	1.925		
120	1.18 1.27	1.225	1.77 2.24	2.005		

* Solidified with sorbent/flyash/lime/Basin F ratio of 1/1/1/1, no sequestering.
 ** ND = No data.

Table 8
Desorption Isotherms for
Solidified Basin F Liquid*

<u>Sorbent</u>	<u>L/S</u>	<u>Liquid ml</u>	<u>Solid g</u>	<u>C mg/l</u>	<u>q mg/l</u>	<u>K_d</u>	<u>r</u>
Soil	100	100	1	1.0065	0.70735	0.3562	0.9996
	50	50	1	1.1555	0.750225		
	25	50	2	3.32	1.45		
	10	50	5	9.11	3.5845		
S/S-1.5w	100	100	1	1.41	0.667	0.4228	0.988
	50	50	1	2.01	0.7075		
	25	50	2	4.295	1.40125		
	10	50	5	8.55	3.6125		
S/S-15w	200	100	0.5	0.943	0.3097	0.6829	0.9914
	100	100	1	1.33	0.675		
	50	50	1	1.93	0.7115		
	25	50	2	3.06	1.463		
	10	50	5	5.94	3.743		

* Solidified with additive ratios of 1/1/1/1, soil/flyash/lime/Basin F liquid.

L/S = Liquid-to-solids ratio.

C = Aqueous phase copper concentration.

q = Solid phase copper concentration.

K_d = Desorption coefficient.

r = Coefficient of determination.

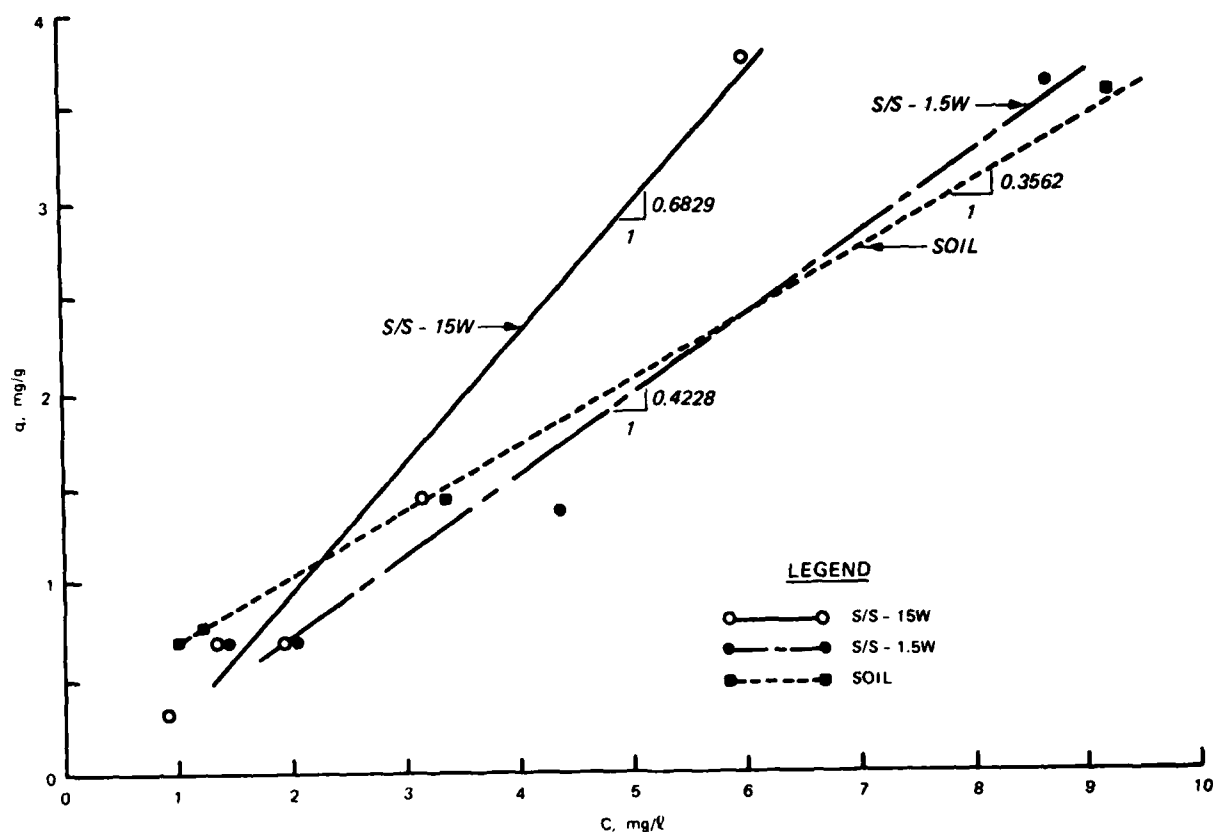


Figure 8. Desorption isotherm curves

sorbent preparation produced a product with a higher K'_d than did sorbent-assisted solidification using a S/S-1.5w sorbent preparation, and the latter produced a product with a higher K'_d than did sorbent-assisted solidification using soil alone. The desorption isotherms show that the affinity of copper for the organosilane reduced the amount of copper in the aqueous phase. The sorbents used in the desorption isotherm tests were not prepared by taking the soil/organosilane mixtures to dryness. The adsorption isotherms in Figure 5 indicate that had sorbent preparation involved taking the soil/organosilane mixtures to dryness, the desorption coefficients probably would have been higher. The problem with bonding procedures was not recognized early enough in the testing program to include sorbents prepared by taking the mixture to dryness in the desorption isotherm testing.

Uniform leach procedure

52. The ULP data for four solidified products are presented in Table 9. Two solidification processes were used to develop the four products. One of

Table 9
Uniform Leach Procedure Results

Day	Additive Ratio*	Sorbent	SR	Copper Concentration mg/l		
				A	B	Ave.
1	1/1/1/1	Soil	0	10.5	8.98	9.74
		S/S-1.5w	0	7.07	7.47	7.275
	0.7/0.7/0.7/1	Soil	1.15	0.088	0.094	0.091
		S/S-1.5d	1.15	0.082	0.087	0.0845
	1/1/1/1	Soil	0	4.27	4.15	4.21
		S/S-1.5w	0	3.19	3.1	3.145
2	0.7/0.7/0.7/1	Soil	1.15	0.208	0.127	0.1675
		S/S-1.5d	1.15	0.052	0.051	0.0515
	1/1/1/1	Soil	0	1.6	2.17	1.885
		S/S-1.5w	0	2.72	1.43	2.075
	0.7/0.7/0.7/1	Soil	1.15	0.234	0.2	0.217
		S/S-1.5d	1.15	0.024	0.042	0.033
4	0.7/0.7/0.7/1	Soil	1.15	0.173	0.176	0.1745
		S/S-1.5d	1.15	0.066	0.062	0.064
5	0.7/0.7/0.7/1	Soil	1.15	0.121	0.175	0.148
		S/S-1.5d	1.15	0.134	0.164	0.149
6	0.7/0.7/0.7/1	Soil	1.15	0.092	0.063	0.0775
		S/S-1.5d	1.15	0.144	0.16	0.152

* 1/1/1/1 Soil, Bulk Wt of A = 1,672 g, B = 1,642 g.
 1/1/1/1 S/S-1.5w, Bulk Wt of A = 1,647 g, B = 1,633 g.
 0.7/0.7/0.7/1 Soil, Bulk Wt of A = 1,560 g, B = 1,572 g.
 0.7/0.7/0.7/1 S/S-1.5d, Bulk Wt of A = 1,583 g, B = 1,556 g.

the solidification processes included the use of ammonia sequestering reagents (SR = 1.15) and the other did not. Two variations on each process were tested. In one, organosilane-conditioned soil was used as a solidification reagent and in the other unconditioned soil was used. The ULP tests were terminated due to spalling after three leaching cycles for the solidification process that did not use sequestering reagents and after six leaching cycles for the processes that included sequestering reagents. These data are plotted in Figure 9. The data show that both organosilane conditioning of the soil and the use of ammonia sequestering reagents reduced the leaching of copper

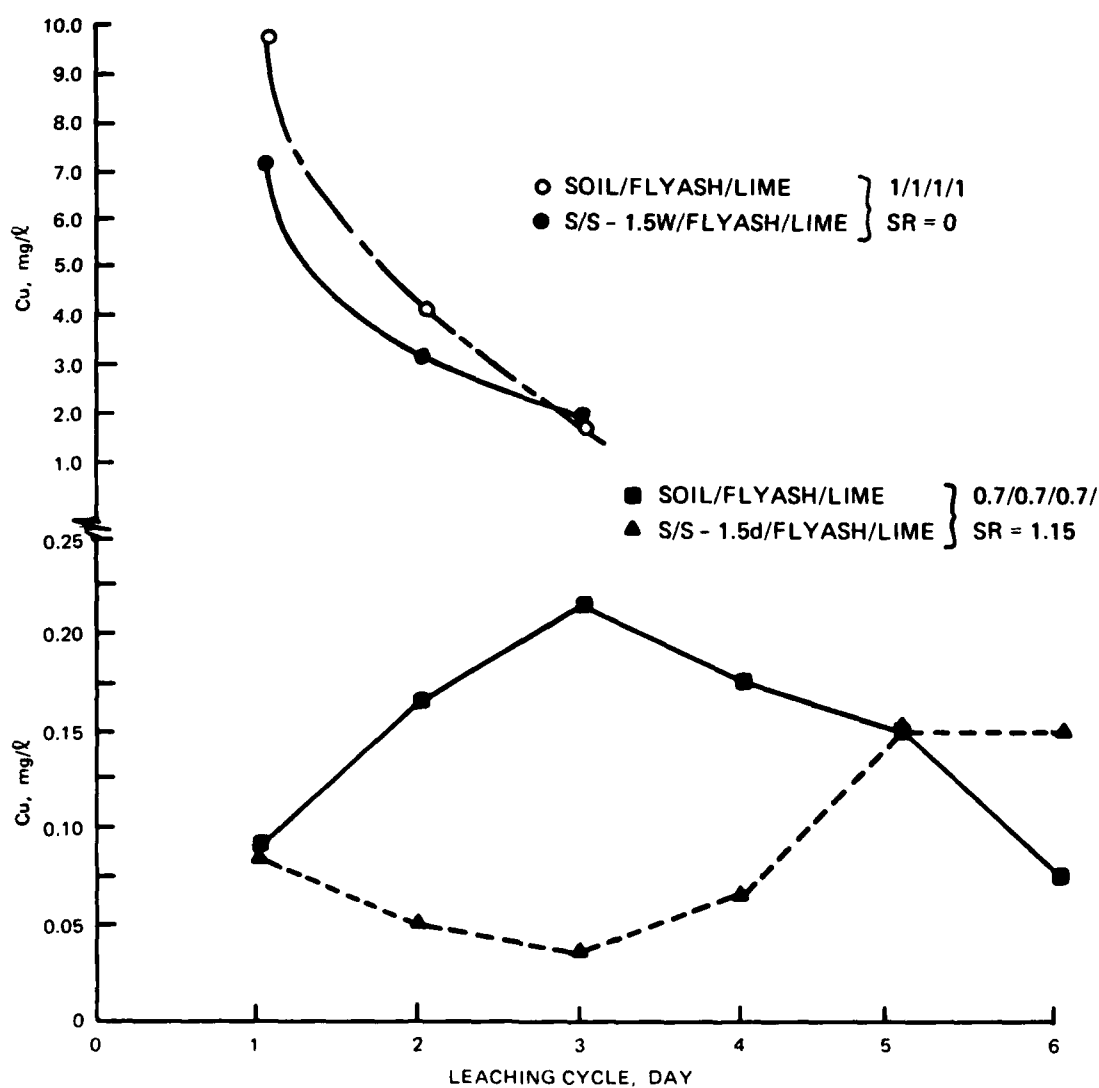


Figure 9. Plot of uniform leach procedure results

under the conditions of the ULP. The use of sequestering reagents and organosilane-conditioned soil together in the same process formulation combined to reduce the initial levels of copper in ULP leachates. As spalling of the samples proceeded with each leaching cycle, the leachate copper concentrations from the product with organosilane conditioning plus ammonia sequestering began to equal and then exceed the leachate copper concentrations from the product prepared with ammonia sequestering and unconditioned soil. The order of copper leaching was: 1/1/1/1 (soil/flyash/lime/Basin F liquid) > 1/1/1/1 (soil-organosilane/flyash/lime/Basin F liquid) > 0.7/0.7/0.7/1 (soil/flyash/lime/Basin F liquid) with sequestering reagents > 0.7/0.7/0.7/1 (soil-organosilane/flyash/lime/Basin F liquid) with sequestering reagents. These data parallel the trends in the previously discussed EP and desorption isotherm tests. The EP and desorption isotherm tests showed that products prepared using organosilane-conditioned soil are less leachable than those prepared using unconditioned soil, except when used in combination with sequestering reagents. In the early stages of the ULP the reverse was true. In the later leaching cycles of the ULP, copper concentrations were higher in leachates from the product prepared with ammonia sequestering plus organosilane-conditioned soil than in the product prepared with sequestering and no organosilane conditioning of the soil.

53. The differences between leachates from early and later stages in the ULP were probably due, in part, to differences in exposed surface area caused by differences in spalling. The products prepared using sequestering reagents were more resistant to spalling than the products prepared without ammonia sequestering. The use of organosilane also reduced the degree of spalling. The product prepared using sequestering reagents and organosilane conditioning of the soil was more resistant to spalling than any of the other products tested. In the later stages of the ULP the relative degree of spalling between products was not significant, although significant spalling had occurred in all test specimens. Thus, in the initial cycles of the ULP, the exposed surface areas for leaching were unequal among samples. The lowest leachate copper concentrations were associated with specimens with the least amount of spalling. In the later leaching cycles the differences in spalling were smaller and had less impact on leachate copper concentrations. Since copper leaching was less from spall-resistant products, the ULP data indicate

that the development of a product with good physical integrity is important to reduction of leaching potential.

54. No attempt was made to calculate effective diffusivity for the solidified waste by fitting the ULP data to Equation 4. The ULP tests in this study did not satisfy all the boundary conditions and assumptions necessary for Equation 4 to apply. Due to spalling, the surface area available for leaching varied throughout the tests. Without a fixed surface boundary, the semi-infinite medium assumption does not apply. During the conduct of the ULP, a distinct stratification of clear liquid above the top of the solidified waste specimens and yellow liquid below the top of the solidified waste specimens in the ULP apparatus was observed in each leaching cycle. The yellow color was indicative of the soluble organics in Basin F liquid that were being leached from the solidification products. This well-defined stratification indicated that concentration gradients were present in the leaching medium that limited diffusive transport of material from within the solid to the surface boundary. Resistance to transport across the surface boundary violates an important condition that is necessary for Equation 4 to apply.

Extrapolation of Laboratory Leach Data to the Field Situation

55. Delisting petitions require detailed documentation of proposed treatment alternatives and technical justification for predicted reductions in disposal hazards. Laboratory leaching tests are used to develop this information. Leachate quality is, for example, indicative of the effectiveness of solidification as a contaminant immobilization technology. However, in order to make judgments as to the effectiveness of contaminant containment, a thorough understanding of the potential behavior of solidified waste in the field situation is required.

56. The technical basis for extrapolating laboratory leach data to the field situation depends on the type of leach test. Three types of leaching tests have been discussed in this report, the EP, the ULP, and desorption tests (kinetic and isotherm). A discussion of the technical basis for extrapolating data from each of these leach tests to the field situation follows. It is realized that a number of test conditions may affect the outcome and interpretation of a leaching test, but testing details such as pH, ionic strength, and liquid/solids ratio while important parameters, will not be

dealt with here. Emphasis will be placed on the fundamental basis for extrapolating laboratory data from the three types of leaching tests used in this study to the field situation. It is assumed a priori that extrapolations can be made with greater confidence if they are made from theoretical considerations that satisfactorily model leaching behavior in laboratory systems.

Extrapolation of EP leach data

57. The EP is a criteria-comparison type test in which leachate concentrations from a standardized leaching test are compared with a specific set of criteria. The major advantages of criteria-comparison type tests include cost, screening potential, and established regulatory interpretation. Because this type of test does not provide information on kinetics or on distribution coefficients, the results are difficult to extrapolate to the field situation (Conway and Malloy 1981). In most applications it is assumed that the data correlate to the field situation, but the correlation functions are site specific and are not known.

Extrapolation of ULP data

58. Interpretation of ULP leach data and application of the interpretations to the field disposal situation can be based on the systematic application of mass-transport theory (Godbee and Joy 1974; Godbee et al. 1980). The partial differential equation from which Equation 4 was derived is given below:

$$\frac{\partial C}{\partial t} = \frac{\partial (D_e \partial C / \partial z)}{\partial z} \quad (7)$$

where

C = solid phase contaminant concentration, M_c/L^3

t = time

D_e = effective diffusivity, L^2/T

z = distance from a surface boundary, L

Equation 7 is a classical Fickian diffusion equation. In this equation, leaching is modeled as being controlled by the rate of internal diffusion of contaminant to the surface of a monolithic solid where leaching takes place. The basic assumptions that apply are as follows:

- a. The contaminant of interest is contained in a monolithic solid.
- b. The hydraulic conductivity of the solid is negligible (convective transport is not considered).
- c. The solid mass has a surface boundary exposed to a leaching medium.
- d. The contaminant must be at the exposed surface in order to be leached.
- e. The contaminant reaches the surface boundary by internal diffusion from within the waste-containing solid.
- f. Once at the surface there is no resistance to contaminant release to the leaching medium so that the contaminant concentration at the surface is always zero.

59. By fitting ULP data to a model equation, such as Equation 4, effective diffusivity D_e can be determined. The effective diffusivity accounts for pore phenomena specific to each solidified product and each contaminant. It is a material property of the solidified waste like density or specific heat that can be used to make long-term inferences about the performance of products in the field using Equation 7.

60. When considering the use of model equations such as Equation 4, it is important to realize that without initial and boundary conditions, Equation 7 has no solution, and that the solution depends on the initial and boundary conditions that are imposed. Few if any field disposal situations for solidified waste will satisfy all the constraints of the initial and boundary conditions stated above. The ULP is best applied to dense, virtually impermeable solidified waste in which solid-phase diffusion is the predominant leaching mechanism. Long-term predictions of contaminant flux at the monolith boundaries based on Equation 7 could be overly conservative if hydrologic processes become significant.

Extrapolation of desorption isotherm data

61. For materials that are not appropriate candidates for ULP testing, desorption tests can be used to provide fundamental information on transfer processes that control solid-liquid interactions. This information can then be used in a mass-transport model to simulate the field situation. The one-dimensional mass-transport equation for a permeant in a porous media is given by Equation 8 below (Lapidus and Amundson 1952; Hornsby and Davidson 1973; Lowenbach et al. 1977; Rao et al. 1979; Grove and Stollenwork 1984):

$$\partial C / \partial t = -\partial(vC) / \partial z + D_p (\partial^2 C / \partial z^2) - \frac{\rho}{\theta} \left(\frac{\partial q}{\partial t} \right) \quad (8)$$

where

- C = contaminant concentration in the leachate, M_c / L^3
- v = seepage velocity, L/T
- D_p = dispersion coefficient, L^2/T
- z = space dimension, L
- ρ = bulk density of solidified waste, M_s / L^3
- θ = volumetric water content, L^3 / L^3
- q = contaminant concentration in solid phase, M_c / M_s

Equation 8 is an aqueous phase equation. The first term $\partial(vC)/\partial z$ is the bulk flow term. This term accounts for convective transport by a flowing medium. The second term $D_p (\partial^2 C / \partial z^2)$ accounts for mechanical dispersion and molecular diffusion in the aqueous phase. The third term $\rho/\theta (\partial q / \partial t)$ is the source term for contaminant desorption from the solid phase into the aqueous phase. For the desorption isotherms run in this study, the source term in Equation 8 will take the form given below:

$$\frac{\rho}{\theta} \left(\frac{\partial q}{\partial t} \right) = \frac{\rho K_d}{\theta} \left(\frac{\partial C}{\partial t} \right) \quad (9)$$

62. For the materials tested in this study, Equation 8 is an appropriate partial differential equation (PDE) and Equation 9 is the appropriate expression for the source term. This PDE can be solved by numerical approximation on a computer. Specific data pertaining to the solidified waste, e.g. permeability and void volume ratio, and other factors that are site specific such as infiltration rate, are required in order to apply Equation 8. Information provided by computer approximation of Equation 8 can be used to support delisting petitions as technical input to planning level assessments of proposed solidification/landfill projects, and to assess the probable effectiveness of alternative control strategies for reducing environmental impacts.

Potential For Field Application

63. Several aspects of field application were beyond the scope of this investigation. These include scale-up factors, organosilane compatability with alternative binder/substrate systems, long-term stability of the solidified product, and engineering economy. Additional testing and evaluation are needed before organosilane-assisted solidification can be applied in the field.

64. In addition, organosilanes are produced as speciality chemicals that are expensive in small quantities. Even with a significant cost breakthrough between laboratory and bulk quantities, full-scale application of sorbent-assisted solidification using organosilane may be limited to small volumes of highly contaminated metal wastes that would otherwise pose a serious environmental hazard if landfilled.

PART V: CONCLUSIONS AND RECOMMENDATIONS

Conclusions

65. A laboratory investigation of sorbent-assisted solidification of liquid from a hazardous waste lagoon at the Rocky Mountain Arsenal was conducted. Adsorption isotherms and chemical leach tests were used to obtain information on the contaminant immobilization properties of solidification using various sorbents. The feasibility of improving the natural adsorptive capacity of soil by conditioning with N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane was investigated. Metal immobilization mechanisms for solidified waste were discussed. Theoretical results were presented that concern the technical basis for extrapolation of laboratory leach data to the field situation. The scientific basis for field extrapolation of three leach tests was evaluated.

66. Sorbent-assisted solidification is an innovative treatment technology that could be applied, depending on technical and economic factors associated with full-scale application, to highly contaminated metal wastes that would otherwise pose a serious environmental hazard if landfilled. The basis of the system is adsorption/chemisorption of metals to a sorbent that, used in conjunction with a solidification processing system, can reduce the pollutant potential of metals in hazardous wastes. Organosilane conditioning of selected additives in a process formulation to make solidified waste more resistant to chemical leaching can be effective when applied within constraints related to chemical compatibility of the organosilane with the solidification additives. With the proper development and application, sorbent-assisted solidification could represent an improved treatment technology that could be applied to highly contaminated metal wastes prior to land disposal.

67. Specific conclusions drawn from the evaluation of the information obtained in this study are as follows:

- a. For the flyash and soil tested in this study, organosilane-conditioned soil was a better copper sorbent than organosilane-conditioned flyash.
- b. The natural adsorptive capacity of the soil was improved by conditioning the soil with N-(β -aminoethyl)- γ -aminopropyl-trimethoxysilane.

- c. Soil/organosilane bonding procedures as well as organosilane dosage affect sorbent performance. When the soil/organosilane mixture was not taken to dryness, the sorbent produced was inferior to that produced when the mixture was taken to dryness.
- d. Organosilane conditioning of the soil additive lowered the leachability of copper from solidified Basin F liquid in three different leaching tests, the EPA toxicity extraction procedure, the uniform leach procedure, and in batch desorption tests.
- e. The use of ammonia sequestering reagents lowered the leachability of copper from solidified Basin F liquid.
- f. The combined effect of sequestering reagents and organosilane conditioning of the soil was to increase the leachability of copper for solidified Basin F liquid.
- g. Copper leachability was less from spall-resistant products. The development of a product with good physical integrity is important to reduction of leaching potential.
- h. The field application of chemical leach data obtained in laboratory testing is highly dependent on the design of the leach test and the method of interpretation.

Recommendations

68. Sorbent-assisted solidification using organosilane is an innovative treatment technology for wastes containing toxic metals. Due to the developmental nature of the technology, additional testing is required before organosilane-assisted solidification is applied in the field. Additional testing should address the following topics:

- a. Potential use of other organosilanes and other substrates for developing sorbents, e.g., sand.
- b. Long-term stability of organosilane-conditioned sorbents.
- c. Compatibility of organosilane-conditioned sorbents with various solidification agents, e.g., portland cement.
- d. Development of improved organosilane-substrate bonding procedures.
- e. Economic feasibility of full-scale application.

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APPENDIX A: FLYASH POZZOLAN REPORT

This appendix presents results from pozzolan tests performed on the fly-ash used in this study. The tests were conducted by the Cement and Pozzolan Unit, Structures Laboratory, US Army Engineer Waterways Experiment Station. The Cement and Pozzolan Unit's report is provided as Plate A1.

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